

Ab Initio Compact Group Model Potentials for Describing Environment Effects in Cluster Calculations

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ABSTRACT: A method for the determination of *ab initio* group model potentials within the Hartree–Fock framework is reported. Following the theory of separability of many electron systems, a new way to incorporate the effect of complete chemical entities by means of polycenter compact model potentials is presented. The interaction between active and frozen electrons is partitioned as a sum of long- and short-range terms. The long-range term is described as the effect of $-2e$ charges placed in the center of the charge of the frozen group molecular orbitals; the short-range one, the exchange and Pauli repulsion, is developed as a spectral representation in a nonorthogonal basis set. An algorithm to solve the problem associated with the rotation of the polycenter model potential is presented and implemented in an all-purpose quantum chemical program. In order to check the method, a group model potential for H₂O was obtained and tested. © 1999 John Wiley & Sons, Inc. *J Comput Chem* 20: 1145–1152, 1999

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Introduction

One of the most successful approximations used in quantum chemistry, which is intended to reduce the huge computational effort

necessarily involved, is to classify the electrons of a given system as active or inactive.^{1–4} Within an *ab initio* framework, the most widely used technique in this sense is the replacement of inner atom electrons by an effective core potential (ECP) under a variety of theoretical formulations. The main idea underlying this is to consider that core electrons can be assumed to behave as spectators and therefore can be frozen. This concept is not exclusive for core electrons; in fact, it can also be employed to describe the behavior of atoms or

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ions to model the effects of the environment in cluster embedded calculations.⁵ In these cases, because of spherical symmetry, the computational task can be straightforwardly set up as an extension of the well-known ECP strategy. Obviously, to extend this type of methodology to nonspherical groups is a much more complicated task, although, if successful, the applicability of this type of effective group potentials would be of major interest to describe the ambient of active sites in enzymes, zeolites, surfaces, etc., or to incorporate solvent effects in those cases where the conventional cavity model is not appropriate.

Despite this interest, only a few works addressed this subject. These developments were in two essential directions. In the first the efforts were concentrated on the determination of effective potentials for fragments that could be employed as saturator groups. Thus, effective potentials for NH_3 ,⁶ SiH_3 ,⁷ and COOH ⁸ were reported. The underlying idea here is just like that of the ECPs where nonactive electrons on the *same* molecular entity are avoided. In the second direction the potential is intended to replace a complete molecule or group in calculations in which the environment is described through an embedding type technique. Along this line, in 1993 Mejías and Sanz⁹ reported about the determination of *ab initio* group model potentials (GMPs) for HF molecule, together with some applications. Such GMPs were derived following a formalism similar to that of the *ab initio* environment model potential method (AIEMP) proposed by Barandiarán and Seijo,⁵ but extended to polycenter groups. Later, Frank et al.¹⁰ reported on the feasibility to represent spectator molecules through effective potentials generated in a semiempirical NDDO calculation. More recently, Day et al.¹¹ developed a method to obtain what they called an "effective fragment model" that makes use of a distributed multipole expansion that allowed them to replace water molecules by an effective potential. Excellent results were reported.¹²

In the present work we report on a further development of our previous work on GMPs that is intended to both systematize its determination and speed up the computation of the gradients through derivation and implementation of analytical formulae. As reported in ref. 9, the Coulomb operator for a given group was handled by fitting its electronic density using a reduced set of Gaussian functions; the molecular integrals were computed using a basis set spanned into a lobe Gauss-

ian representation. Although this strategy permits one to solve the problem of one-electron integral computation, its general applicability is limited. To overcome this limitation, a spectral representation for the model potential was later used. Such a representation gives rise to an easy and fast calculation of one-electron integrals, as well as their contribution to the analytical gradient; it was used to determine compact model potentials for closed¹³ and open shell¹⁴ ions (one-center groups) intended to describe the environment in embedding cluster calculations. The purpose of the present work is to extend this technique to the description of polycenter groups. It should be noted that an efficient implementation of group effective potentials to describe complete molecules needs to solve the problem of the rotation that may occur for a specific situation. That is why this aspect will constitute a significant part of this work. The article is arranged as follows: a brief overview of the theoretical frame is given; the rotation of the GMP, as well as their contribution to the analytical gradient, is described; some test calculations are reported (more extensive application will be presented in a forthcoming work); and the main conclusions are summarized.

Theoretical Foundations

The theoretical foundation are reviewed elsewhere; consequently, only a brief summary is given here. Let us assume that a system can be partitioned into two subunits according to the theory of separability of a many electron system of McWeeny and Kleiner,^{1,15} and Huzinaga et al.²⁻⁴ The first subunit (i.e., the active group or cluster) consists of a set of nuclei and electrons that we are interested in describing. The second subunit or *environment* is constituted of a set of nuclei and electrons that can be considered as spectators and can therefore be frozen. The total electronic wave function of the system can be written as

$$\Phi = M\hat{A}(\Psi_{\text{clus}}\Psi_{\text{env}}), \quad (1)$$

where M is a normalization factor and \hat{A} is the antisymmetrizer between the cluster and the environment. These wave functions are assumed to fulfill the strong orthogonality condition¹⁶:

$$\int \Psi_{\text{clus}}(1, i, j, \dots) \Psi_{\text{env}}(1, k, l, \dots) dx_1 = 0. \quad (2)$$

The environment wave function can also be approximated as an antisymmetrized product of one-determinant group wave functions representing A, B, C, \dots , groups, each one with N_A, N_B, N_C, \dots , electrons¹⁵; then we can express

$$\Psi_{\text{env}} = M' \widehat{A}(\Psi_A \Psi_B \dots) \quad (3)$$

and all group wave functions are strongly orthogonal.

According to eq. (1), the total energy of the system can be written as

$$E = E_{\text{clus}} + E_{\text{env}} + E_{\text{clus-env}}. \quad (4)$$

Because the environment is assumed to be frozen, the relevant quantities in eq. (4) are the energies of the cluster and the cluster–environment interaction; therefore, we can define an *effective energy* as

$$E_{\text{eff}} = E_{\text{clus}} + E_{\text{clus-env}}. \quad (5)$$

Following eq. (3), the interaction energy with the environment is written as

$$E_{\text{clus-env}} = \sum_{I \in A, B, C \dots} E_{\text{clus-I}}, \quad (6)$$

where each addition is given by

$$\begin{aligned} E_{\text{clus-I}} = & \langle \Psi_{\text{clus}} | \widehat{V}_I | \Psi_{\text{clus}} \rangle \\ & + \langle \Psi_{\text{clus}} | - \sum_{j=1}^{j=N_I} \frac{Z_j^I}{|r - R_j^{\text{clus}}|} | \Psi_{\text{clus}} \rangle \\ & + \langle \Psi_I | - \sum_{j=1}^{j=N_{\text{clus}}} \frac{Z_j^{\text{clus}}}{|r - R_j^{\text{clus}}|} | \Psi_I \rangle \\ & + \sum_{i=1, j=1}^{i=N_I, j=N_{\text{clus}}} \frac{Z_j^{\text{clus}} Z_i^I}{|R_i^I - R_j^{\text{clus}}|}. \end{aligned} \quad (7)$$

The first and second term on the right-hand side of eq. (7) accounts for the interaction between cluster electrons and the electrons and nuclei of environment group I , respectively; the third refers to the interaction between cluster nuclei and environment electrons; and the fourth term concerns electrostatic repulsion between cluster and environment nuclei.

To solve for Ψ_{clus} only the first two terms of eq. (7) are needed; the last two contributions are added after convergence of the self-consistent field (SCF) procedure. Therefore, the effective Fock operator

introducing the cluster–environment interaction is

$$\widehat{F} = \widehat{F}_0 + \sum_{I \in \text{env}} \left[\widehat{V}_I - \sum_{j=1}^{j=N_I} \frac{Z_j^I}{|r - R_j^I|} + \widehat{P}_I \right], \quad (8)$$

where \widehat{P}_I is a weighted projection operator over occupied orbitals of group I that allows for restriction of the variational space to the Fock cluster space:

$$\widehat{P}_I = \sum_{j=1}^{j=\text{occ}} |\varphi_j^I\rangle \langle -x_j^I \varepsilon_j^I| \langle \varphi_j^I|, \quad (9)$$

where j runs over the occupied molecular orbitals φ_j^I of I with eigenvalues ε_j^I . The projector factor x_j^I is set to its theoretical value of 2.¹⁷

On the other hand, the operator \widehat{V}_I representing the electronic interaction between two groups is

$$\widehat{V}_I = \sum_{i=1}^{i=\text{occ}} \left(2\widehat{J}_i^I - \widehat{K}_i^I \right), \quad (10)$$

where

$$\widehat{J}_i^I = \int \varphi_i^I(2) \frac{1}{r_{12}} \varphi_i^I(2) dr_2 \quad (11)$$

and

$$\widehat{K}_i^I = \int \varphi_i^I(2) \frac{1}{r_{12}} dr_2 \widehat{p}_{12} \varphi_i^I(2). \quad (12)$$

In order to avoid the evaluation of two-electron integrals connecting cluster and environment atomic orbitals, the usual simplification is to simulate \widehat{J}^I and \widehat{K}^I operators through simple functionals. The most practical way^{5,18} to account for the non-local exchange operator \widehat{K}^I is based on a nondiagonal spectral representation according to which

$$\widehat{K}^I \cong \sum_i \sum_j |g_i^I\rangle C_{ij} \langle g_j^I|. \quad (13)$$

The C_{ij} coefficients are the matrix elements in

$$C = \left(S_g^I \right)^{-1} K_g^I \left(S_g^I \right)^{-1} \quad (14)$$

and

$$\left(K_g^I \right)_{i,j} = \langle g_i^I | \widehat{K}^I | g_j^I \rangle, \quad (15)$$

where g_i^I being the set of primitive functions used to describe group I .

The usual way of accounting for the Coulomb operator \widehat{J} , is to fit either the electronic density or directly the potential by a functional in which the

parameters are adjusted to reproduce the radial dependence of the potential. For nonspherical potentials, such a technique leads to a fit in a 4-dimensional grid and therefore an extremely large number of points is involved. This problem was overcome in ref. 9 by using a procedure based on the simplified representation of potentials produced by the Gaussian charge distributions of Fortunelli and Salvetti.¹⁹ However, as stated in the Introduction, this procedure gives rise to the evaluation of difficult integrals, mainly when rotation and gradient contributions of the model potential are considered. An alternative way to circumvent these technical difficulties makes use of a spectral representation of the Coulomb operator. Because it was shown that this type of representation can be used if the potential is a short-range one, we chose (as reported in ref. 13) to divide the electronic contribution into short- and long-range contributions. In this way, compact model potentials (CMPs) were determined for a number of ions and analytical formulae for the gradients were developed and implemented in an all-purpose molecular quantum mechanics program (HONDO 8.4).²⁰

To obtain compact GMPs we followed a similar strategy consisting of partitioning the electronic operator \hat{V}_I in short- and long-range contributions,

$$\hat{V}_I \approx \hat{W}^I = \hat{W}_{\text{LR}}^I + \hat{W}_{\text{SR}}^I, \quad (16)$$

obtaining the spectral representing for \hat{W}_{SR}^I . Taking into account that our *environment* consists of closed shell groups, we can assume that the electronic cloud of group I can be viewed as a long distance as a distribution of charges with a value of $-2e$ located in the center of charge, R^{cc} , for every occupied orbital φ_i^I . It is not difficult to see that this distribution corresponds to the electric dipole moment of environment electrons. The long-range potential \hat{W}_{LR}^I is written

$$\hat{W}_{\text{LR}}^I = \sum_{i=1}^{i=N_I/2} \frac{-2e}{|r - R^{\text{cc}, I_i}|} \quad (17)$$

For the short-range potential

$$\hat{W}_{\text{SR}}^I = \hat{V}_I - \sum_{i=1}^{i=N_I/2} \frac{-2e}{|r - R^{\text{cc}, I_i}|} = \sum_{i,j} |g_i^I\rangle U_{i,j}^I \langle g_j^I|, \quad (18)$$

the last term being the spectral representation on the basis set of primitive function $\{g_i\}$. In the case of a spherical group (i.e., an atom or ion), the

potential \hat{W}_{LR}^I thus selected almost cancels out the Coulomb repulsion and all the charges would be at the coordinates origin in which the environment was solved, just like the CMP implementation.¹³

Notice that this procedure is similar to that proposed by Katsuki⁸ to simulate functional groups in which the representation of the electronic operator \hat{V}_I was achieved by subtracting and adding to $2\hat{J}^I - \hat{K}^I$ an operator \hat{V}_{ad}^I , in such a way that $2\hat{J}^I - \hat{V}_{\text{ad}}^I \approx 0$. For the operator \hat{V}_{ad}^I Katsuki⁸ selected the form

$$\hat{V}_{\text{ad}}^I = - \sum_a \frac{Z_a^I}{|r - R_a^I|},$$

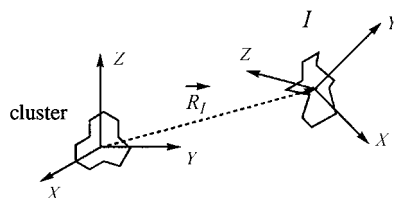
accounting for the interaction with the extended Mulliken charges.

Rotation of GMPs

Once the form of operator \hat{V}_I is defined, we must deal with the rotation of the GMP, which constitutes the main goal of this article. Using eqs. (9) and (16), and after spanning the molecular orbitals (MOs) φ_i^I on the g_i^I basis set, eq. (8) transforms into

$$\hat{F} = \hat{F}_0 + \sum_{I \in \text{ent}} \left[\sum_{i,j} |g_i^I\rangle D_{i,j}^I \langle g_j^I| - \sum_{j=1}^{j=N_I} \frac{Z_j^I}{|r - R_j^I|} + \sum_{i=1}^{i=N_I/2} \frac{2e}{|r - R^{\text{cc}, I_i}|} \right], \quad (19)$$

where $D_{i,j}^I$ combines the short-range and projection operators. Let us assume that for a given group I , we have solved for the coefficients $D_{i,j}^I$ and the vectors R^{cc, I_i} , taking as data the nuclear coordinates R_j^I referenced to the axis system γ in which the model potential is obtained. When solving for the cluster, we find that group I is displaced to position \vec{R}_I and rotated with respect to the system of the cluster.



Translation and rotation can both be easily incorporated into the last two terms of eq. (19) by knowing the unit vectors $\vec{e}_x^I, \vec{e}_y^I, \vec{e}_z^I$ specifying the direction of axis γ with respect to the cluster origin because any vector in γ , labeled \vec{r}^γ , is connected to this representation in the cluster system according to

$$\vec{r}^{\text{clu}} = \vec{R}_I + \vec{B} \cdot \vec{r}^\gamma, \quad (20a)$$

$$\vec{r}^\gamma = \vec{B}^{-1} \cdot (\vec{r}^{\text{clu}} - \vec{R}_I), \quad (20b)$$

where

$$(\vec{B})_{i,j} = \vec{e}_i^{\text{clu}} \cdot \vec{e}_j^I, \quad i, j = x, y, z.$$

However, solving for the spectral representation part of eq. (19) is not so straightforward because it involves the calculation of overlap integrals, $\langle g_i^I | f_j^{\text{clus}} \rangle$, between functions referenced with respect to rotated systems. Both group g_i^I and cluster f_j^{clus} basis functions are, in general, Gaussian functions of the form

$$f(\alpha_j, \vec{l}_j, \vec{R}_j) = \exp\left(-\alpha_j(\vec{r} - \vec{R}_j)^2\right)(x - R_{jx})^{l_{j1}} \times (y - R_{jy})^{l_{j2}}(z - R_{jz})^{l_{j3}} \quad (21)$$

and

$$g(\beta_i, \vec{l}_i, \vec{R}_i^{\gamma I}) = \exp\left(-\beta_i(\vec{r}^\gamma - \vec{R}_i^{\gamma I})^2\right)(x^\gamma - R_{ix}^{\gamma I})^{l_{i1}} \times (y^\gamma - R_{iy}^{\gamma I})^{l_{i2}}(z^\gamma - R_{iz}^{\gamma I})^{l_{i3}}. \quad (22)$$

To solve for the integrals $\langle g_i^I | f_j^{\text{clus}} \rangle$ we first have to express g_i^I in the cluster system. From eq. (18) we have $\vec{r}^\gamma - \vec{R}_i^{\gamma I} = \vec{B}^T * (\vec{r} - \vec{R}_i^I)$ and, because matrix \vec{B} is unitary

$$(\vec{r}^\gamma - \vec{R}_i^{\gamma I})^2 = (\vec{r} - \vec{R}_i^I)^2. \quad (23)$$

On the other hand

$$x^\gamma - R_{ix}^{\gamma I} = B_{1,1}^T(x - R_{ix}^I) + B_{1,2}^T(y - R_{iy}^I) + B_{1,3}^T(z - R_{iz}^I), \quad (24)$$

$$y^\gamma - R_{iy}^{\gamma I} = B_{2,1}^T(x - R_{ix}^I) + B_{2,2}^T(y - R_{iy}^I) + B_{2,3}^T(z - R_{iz}^I), \quad (25)$$

$$z^\gamma - R_{iz}^{\gamma I} = B_{3,1}^T(x - R_{ix}^I) + B_{3,2}^T(y - R_{iy}^I) + B_{3,3}^T(z - R_{iz}^I). \quad (26)$$

Using the Newton binomial expansion and eqs. (23)–(26), the overlap integral is

$$\left[\frac{l_{i1}! l_{i2}! l_{i3}!}{(l_{i1} - k_1)!(k_1 - l_1)! l_1! (l_{i2} - k_2)!(k_2 - l_2)! l_2! (l_{i3} - k_3)!(k_3 - l_3)! l_3!} \right] \times \left[(B_{1,1})^{l_{i1}-k_1} (B_{2,1})^{k_1-l_1} (B_{3,1})^{l_1} (B_{1,2})^{l_{i2}-k_2} (B_{2,2})^{k_2-l_2} (B_{3,2})^{l_2} (B_{1,3})^{l_{i3}-k_3} (B_{2,3})^{k_3-l_3} (B_{3,3})^{l_3} \right] \times \left\langle \eta\left(\beta_i, \vec{l}_i, \vec{R}_i + \vec{B} * \vec{R}_i^{\gamma I}\right) \middle| f_j^{\text{clus}} \right\rangle, \quad (27)$$

where

$$\vec{l}_i' = \begin{pmatrix} l_{i1} + l_{i2} + l_{i3} - k_1 - k_2 - k_3 \\ k_1 + k_2 + k_3 - l_1 - l_2 - l_3 \\ l_1 + l_2 + l_3 \end{pmatrix}. \quad (28)$$

As can be seen, eq. (27) is a combination of $\langle \eta(\beta_i, \vec{l}_i, \vec{R}_i + \vec{B} * \vec{R}_i^{\gamma I}) | f_j^{\text{clus}} \rangle$ integrals usually implemented in the available computational chemistry software. The evaluation of (27) involves a sixth-order summation and therefore such a step is time consuming; however, the computational effort can be reduced by taking advantages of eq. (28) as explained in the Appendix.

The next point concerns the computation of the GMP contribution to the cluster gradient. This task

can be achieved following a procedure similar to that reported in ref. 9, according to which the central point in the present case involves the computation of $\langle g_i^I | f_j^{\text{clus}} \rangle$ derivatives with respect to the cluster nuclear coordinates. These derivatives can be handled following the procedure stated above. Notice, on the other hand, that for the rest of the contributions it is easier to solve with respect to the γ axis system and then to transform the gradient vector back to the cluster reference system.

Finally, these algorithms were implemented in the HONDO program.²⁰ The integrals in the atomic basis were evaluated using the King, Dupuis, and Rys^{21,22} and Gauss–Hermite quadratures. For the computation of the first derivatives of $\langle g_i^I | f_j^{\text{clus}} \rangle$

integrals, the recursive formulae of Obara and Saika²³ were used.

Numerical Examples

This section reports on some numerical examples obtained using a GMP to describe water molecules. More extensive calculations in which the method was used to simulate a cavity in a ZSM5 zeolite will be reported in a forthcoming article.²⁴ The behavior of H₂O GMP was tested by analyzing their suitability to describe the molecular interaction in Hartree-Fock (HF) \cdots H₂O and H₂O \cdots H₂O systems. These test calculations are performed according to the following steps. First, a single calculation of the isolated water molecule was carried out using a fully decontracted basis set.²⁵ To do this, the molecule was centered at the origin of coordinates taking advantage of its symmetry. Second, from the HF MOs, the GMP was determined in the same reference system. Third, the GMP was put in an adequate region of the space, introducing its translation and rotation (if any), and HF and MP2 calculations of the active group or cluster (here HF or H₂O) were then performed. The results were then compared to reference all-electron calculations for the HF \cdots H₂O and H₂O \cdots H₂O systems. All the calculations were performed using a standard TZP basis set.

Two aspects were analyzed in these calculations: the ability of the GMP to correctly reproduce the distances between the clusters and the chemical group, and the shape of the potential surfaces. For the first one we estimated the optimal distances between the active groups and the GMP, as well as their geometries. These results are summarized in Figure 1 and Tables I and II. As can be seen, both the intragroup distances for H₂O and HF are found to be in good agreement, the differences observed at the HF level being 0.005 and 0.05 Å for HF and H₂O, respectively, and somewhat larger at the MP2 level of calculation (0.09 and 0.06 Å). However, it is worth noting that while the MP2 intergroup distance decreases in the all-electron calculations according to the expected hydrogen bridge reinforcement, in the GMP calculation such distances slightly increase. This can be easily understood taking into account that there is no basis set in the GMP region and therefore there is no way to repolarize the electron density in the intergroup region. With respect to the set of intra-

group parameters a good agreement is also observed, and the effects of the electron correlation follow the well-known trends of this small molecules showing that no spurious potentials are introduced by the GMP. The same conclusion can be drawn from the vibrational frequencies reported in the tables. In regard to the shape of the potential surfaces, we plotted the energy profiles versus the active group-GMP distance in Figure 2 together with the all-electron ones shifted by 76.0 hartree. As can be seen there is quite satisfactory agreement between the energy profiles in the minimum and the long distance regions.

Finally, some aspects concerning the computational time benefits are addressed. Taking as a sample the water dimer, the CPU time for an SCF

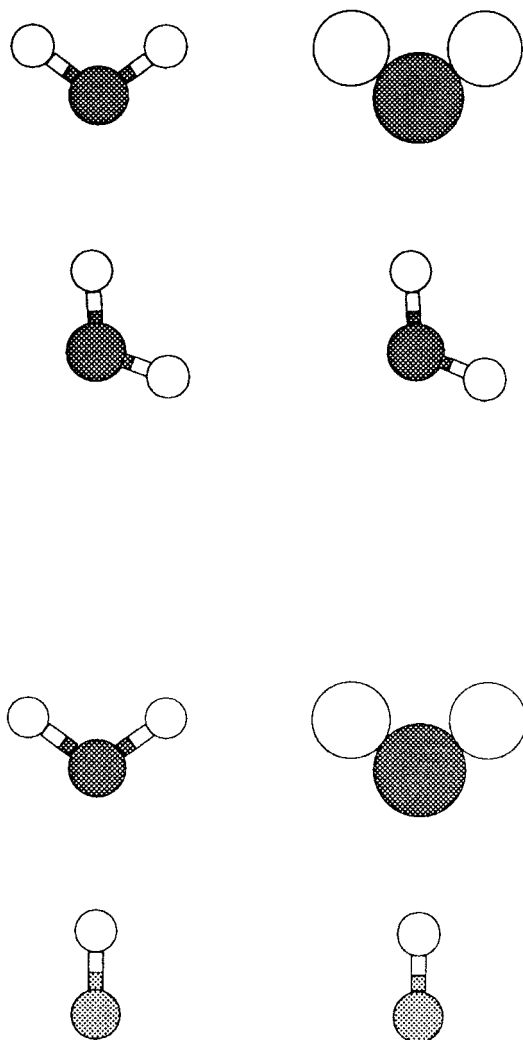


FIGURE 1. Optimized structures for HF \cdots H₂O and H₂O \cdots H₂O systems. Large spheres are intended to describe the H₂O GMP.

TABLE I.
Optimized Distances (d , r) and Vibrational Frequencies (ω) Obtained for $\text{HF} \cdots \text{H}_2\text{O}$ System from All-Electron (AE) and GMP Calculations at Hartree-Fock (SCF) and MP2 Levels.

	AE		GMP	
	SCF	MP2	SCF	MP2
d (Å)	1.793	1.716	1.798	1.810
r (Å)	0.909	0.939	0.898	0.915
ω (cm^{-1})	4178	3842	4474	4252

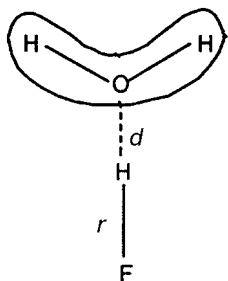


TABLE II.
Optimized Geometries and Vibrational Frequencies (ω) Obtained for $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$ System from All-Electron (AE) and GMP Calculations at Hartree-Fock (SCF) and MP2 Levels.

	AE		GMP	
	SCF	MP2	SCF	MP2
d (Å)	2.022	1.939	1.969	2.001
r_1 (Å)	0.945	0.963	0.938	0.954
r_2 (Å)	0.939	0.956	0.939	0.956
α ($^\circ$)	106.6	104.6	107.4	105.2
ω (cm^{-1})				
asym	4233	3994	4307	4093
sym	4073	3808	4167	3932
bend	1748	1636	1722	1615

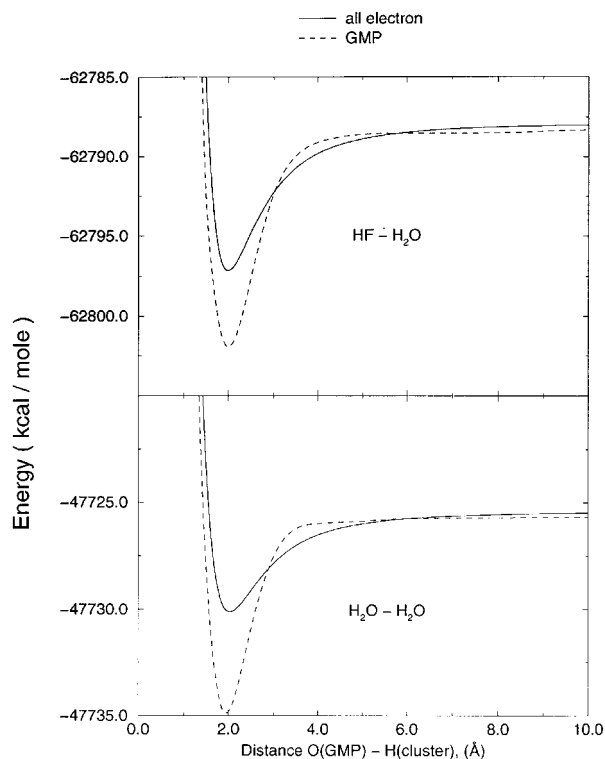
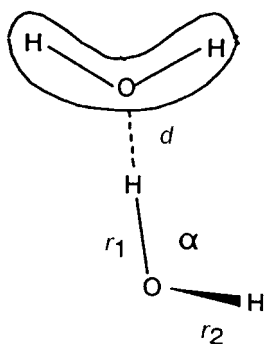


FIGURE 2. Energy profiles for $\text{HF} \cdots \text{H}_2\text{O}$ and $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$ computed from GMP and all-electron (AE) calculations. The all-electron energies have been shifted by 76.0 au.

iteration decreases from 2 s in the all-electron calculation to 0.2 s. For the SCF gradient, the time is lowered from 25.7 to 3.4 s and the MP2 gradient from 36.5 to 5.7 s. In the frequency calculations, the time goes from 2311 to 92 s (times refer to a DEC ALPHA 3900 work station). Of course, this saving is due to the drastic reduction in the number of basis set functions, and it obviously appears that it will be larger for systems in which several chemical groups are modeled by GMPs.

Concluding Remarks

In this work we report on the determination of polycenter GMPs intended to replace molecular entities within an *ab initio* HF framework. The main idea underlying this approach is to constrain the calculation to the active cluster, introducing the effects of surrounding molecules (e.g., a solvent) only in the one-electron part of an effective Fock operator. In order to accomplish this task in a computationally efficient manner (i.e., fast calculation of one-electron integrals and first derivatives),

we followed our earlier implementation for spherical groups, according to which the model potential is partitioned into long- and short-range terms, the latter being incorporated through a nondiagonal spectral representation in a nonorthogonal basis set. Although the computational efficiency of this representation is well established, it exhibits a conspicuous problem related to the rotation of the model potential. The long-range term can be handled in a relatively easy way; for the short-range part we report on an algorithm that, once it is settled down, also allows for a fast calculation of model potential contributions to the cluster gradient. The whole procedure was implemented in an all purpose program (HONDO), permitting us to compute the cluster wave function at the desired level of calculation (MCSCF, MP2, CI, etc.). Preliminary test calculations carried out at the HF and MP2 levels of calculation in which a model potential for H₂O was obtained are also reported and show a satisfactory agreement with reference all-electron calculations.

Appendix

In principle, the calculation of $\langle g_i^l | f_j^{\text{clus}} \rangle$ involves the six sums indicated in eq. (27) and therefore it would lead to the computation of $\langle \eta(\beta_i, \vec{l}_i, \vec{R}_i + \vec{B} * \vec{R}_i^{\gamma l}) | f_j^{\text{clus}} \rangle$ integrals as many times as they appear when the indices are running. These integrals actually depend on \vec{l}_i and the summation are performed according to $l_1, l_2, l_3, k_1, k_2, k_3$ indices for fixed values of l_{i1}, l_{i2}, l_{i3} , which are defined by the wanted $\langle l_i | f_j^{\text{clus}} \rangle$ integral. If eq. (28) is examined, it clearly appears that there is more than one index combination leading to the same vector \vec{l}_i . Therefore, the calculation may be speeded up by computing only the set of unique integrals and putting their value in the appropriate place. The set of unique integrals to be computed is given by

$$\vec{l}_i = \begin{pmatrix} L_1 = 0, 1, 2, \dots, l_{i1} + l_{i2} + l_{i3} \\ L_2 = 0, 1, 2, \dots, L_1 \\ L_3 = 0, 1, 2, \dots, L_2 \end{pmatrix}.$$

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